THE BAND SPECTRUM OF BISMUTH MONOXIDE, (BiO)

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INTRODUCTION

Our knowledge about the spectra of the diatomic oxide molecules of Group V(*b*) elements has been, much extended during the recent years with the lone exception of the BiO molecule. The latest investigation of the spectrum of this molecule seems to be that of Ghosh (1933) who observed a large number of bands in a flaming arc fed with metallic bismuth or bismuth chloride, lying within the region λ4300 to λ6700 and arranged them into four singlet systems. Ghosh followed Mecke and Guillery (1927) in attributing these bands to the diatomic bismuth oxide molecule, BiO, though previous to that Saper (1931) had attributed some of these bands, specially those lying in the shorter wave-length part of the spectrum, to the diatomic chloride, BiCl, as their emitter. Saper's analysis was confirmed first by Morgan (1936) and finally by Roy (1942) who made an extensive investigation of the BiCl band spectrum both in emission and in absorption. The bands in the higher wave-length part of the spectrum ovserved by Ghosh were completely absent in the absorption plates taken by Roy. Though these bands were developed in the emission spectrum of a flaming arc fed with bismuth trichloride in the lower electrode, they could not be incorporated in the BiCl band systems analysed by Roy. Furthermore the chloride isotope effect observable in all the strong BiCl bands was not discernible in the case of these bands. They show moreover, even under the moderate dispersion of a Hilger E. 1 spectrograph, a resolution of the structure lines at the tail parts of the strong bands which is hardly to be expected in the case of bands emitted by such a heavy emitter as BiCl. These considerations lead one to infer that they might be due to the diatomic oxide emitter, BiO.

In analogy with the other oxide molecules of this group (Group V*b*), the ground stage of BiO is expected to be a $^2\Pi$ state and the band systems associated with this state must therefore be double systems. Ghosh analysed them however into singlet systems. Moreover the constants of the ground state evaluated by him are, as has been pointed out by Rochester (1936), smaller than what one should expect for BiO. It was therefore thought desirable to undertake a fresh investigation of the BiO spectrum in order to arrive at a correct vibrational analysis for the evaluation of the molecular constants. This is all the more desirable in view of the fact that a proper correlation of the band systems and constants associated with diatomic oxide molecules of group V(*b*) elements remains incomplete for want of reliable date for BiO.

EXPERIMENTAL

For light source the flame of an arc between bismuth and carbon electrodes as previously used by Ghosh, was employed. Plates for measurements were

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obtained by photographing the bands with a Hilger E52 glass spectrograph as also in the first order of a 6 ft. concave grating on a Paschen mounting. Ilford fine-grained plates were used to obtain the best definition of the band heads. Neon and iron arc lines were photographed for comparison.

Measurements of band heads were carried out with a Gaertner precision comparator (M101) in the usual way. Several sets of measurements were taken. The readings are expected to be correct within 0.1A.

VIBRATIONAL ANALYSIS

The bands discussed in the present communication are all degraded to the red and lie in the region λ5550 to λ6720. All the bands are apparently single-headed and show no existence of double heads even in the spectrograms taken in the first order of a 6 ft. concave grating. From experimental evidence, the emitter of these bands is expected to be the normal diatomic bismuth oxide molecule and we should expect the band systems to arise from transitions between doublet electronic states as in the case of homologous molecules, NO, PO, AsO and SbO. Hence it was first attempted to arrange the bands into two sub-systems. A few trials proved the futility of these attempts and all the bands observed were arranged in a single system, which gave vibrational constants of the right order of magnitude. It seem therefore probable that these bands form only a sub-system of a doublet system, the other sub-system being either on the shorter or on the longer wave length side of these bands. We shall discuss this point more thoroughly in a latter section.

TABLE I

λ in air Å	ν in vacuo in cm.$^{-1}$	(v', v'') Assignment.	λ in air Å	ν in vacuo in cm^{-1}	(v', v'') Assignment.
5563.9	17968	(6,0)	6217.6	16079	(2,0)
5638.5	17730	(7,1)	6299.3	15870	(3,1)
5712.0	17502	(5,0)	6380.0	15670	(4,2)
5786.1	17278	(6,1)	6411.7	15592	(1,0)
5867.9	17037	(4,0)	6495.8	15390	(2,1)
5943.5	16820	(5,1)	6583.0	15186	(3,2)
6022.3	16600	(6,2)	6621.5	15098	(0,0)
6036.9	16560	(3,0)	6710.3	14898	(1,1)
6116.7	16344	(4,1)			

Table I gives the wave lengths in air of all the measured heads, their wave-numbers in vacuo as also the v' v'' – values assigned to each band. Using the wave-number data of the heads, the following equation has been derived in the usual way

$$\nu_h = 15194.5 + \{500.0\,(v'+\tfrac{1}{2}) - 3.10(v'+\tfrac{1}{2})^2\} - \{702.1(v''+\tfrac{1}{2}) - 5.20(v''+\tfrac{1}{2})^2\}$$

The arrangement of the bands referred to above shows that the v' progression (with $v''=0$) bands are fairly strongly developed while of the v'' progression (with $v'=0$) bands, only the first member is present. No trace of the other bands of

this progression was obtained even on our heavily exposed plates. This may be due to the insensitivity of the plates in the region in which these bands are expected to occur. It is found that although the first members of the sequences are fairly strong the sequences themselves are comparatively short. This of course is to be expected from the magnitudes of the vibrational constants which lead one to expect the maximum intensity distribution curve to be a rather wide condon parabola. In the bands under investigation the above seems to be exactly the case, with one limb of the parabola apparently absent.

DISCUSSION

In a recent communication dealing with a new ultra-violet band system of antimony monoxide (SbO), the author (Sen Gupta, 1943) has dealt in some detail with the characteristics of band systems emitted by diatomic oxide molecules of group V(b) elements. There it was shown that the γ-system which is the most prominent and intense amongst the band systems of NO and PO becomes weaker with increasing molecular weight of the emitter. In fact in the case of the SbO molecule, the analogue to the γ-system is so weakly developed that it seems probable as suggested in the above paper, that this band system may not at all be observable in the case of the next higher molecule namely, BiO. As the γ-bands are due to a $^2\Sigma \longrightarrow {}^2\Pi$ transition, their presence would have been indicated by the presence of doubly double-headed bands, which in the case of systems with large doublet separations as expected in the case of BiO, would look like simple double-headed bands. A thorough search of the spectrum emitted by the BiO molecule, has failed, however, to indicate the presence of any such bands. It seems certain, therfore, that the analogue of the γ-band is really too weak to be observed in the case of the BiO molecule at least with methods of excitation and experimental technique which were employed to excite these bands in the case of the other members of the group.

It is now of interest to see whether the BiO bands under investigation have any analogue in the spectra of the other homologous monoxide of group V(*b*) elements. As mentioned earlier, each of the diatomic oxide molecules shows $^2\Pi$ ground state whose separation increases with the increasing weight of emitting molecule, and all the observed band systems of these molecules arise from transitions to this $^2\Pi$ ground state from one or more upper states, which may be either $^2\Sigma$, $^2\Pi$ or $^2\Delta$. As $^2\Sigma \rightarrow {}^2\Pi$ or $^2\Delta \rightarrow {}^2\Pi$ transitions would give rise to double-headed bands, their absence shows that the bands under consideration arise from a transition to the $^2\Pi$ ground state from an upper $^2\Pi$ state. Further it has been mentioned earlier in this paper that these bands could not be arranged into two sub-systems associated with the normal transitions $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}} \rightarrow {}^2\Pi_{\frac{3}{2}}$. One is therefore led to conclude that these bands constitute only a sub-system of a system arising out of a $^2\Pi \longrightarrow {}^2\Pi$ transition.

It is of interest to discuss the whereabouts of the missing sub-system and the causes of its non-appearance. It is now well-known that the doublet inter-

vals in the $^2\Pi$ ground states of NO, PO. AsO and SbO are 121 cm.$^{-1}$, 224 cm.$^{-1}$ 1026 cm.$^{-1}$ and 2272 cm.$^{-1}$ respectively. A separation larger than 2272 cm.$^{-1}$ is therefore expected in the case of BiO. It is now well known that the molecules NS and PO which have the same number of electrons have practically identical doublet separations in their $^2\Pi$ ground levels. The diatomic molecule, with the largest number of electrons, known to have a $^2\Pi$ ground state, appears to be SnCl (Jevons, 1932) having a separation of 2360 cm.$^{-1}$ with 67 electrons, and the largest observed separation in a $^2\Pi$ state is found in the case of HgH molecule, which with 81 electrons, has a $^2\Pi$ state (not a ground state) with a separation of 3684 cm.$^{-1}$. Hence for BiO with 91 electrons the separation of the $^2\Pi$ ground state may be expected to lie between 4000 cm.$^{-1}$ to 4500 cm.$^{-1}$ Now the probable position of the other sub-system could be predicted with some degree of certainty only if the doublet separations of both the states involving in the transition be known. Though we have some idea of the magnitude of the separation in the $^2\Pi$ ground state, it is impossible to form any idea as regards the magnitude of the separation of the upper $^2\Pi$ state. Under the circumstances, the best that we can do is to indicate the region in which the sub-system in question might have occurred assuming a doublet separation in $^2\Pi$ upper state, negligible in comparison with that of the lower $^2\Pi$ state. Assuming the missing sub-system to be the shorter wavelength component, its (0,0) band would occur near 5200Å, while if it be the higher wave-length component, the (0,0) band should occur near 9000Å.

Considering the first alternative, though comparatively strong BiCl bands are present in that region, it is probable that the presence of at least some of the strong bands would have been indicated. But no such bands, not included in the BiCl band spectrum were present in that region, indicating thereby that the missing sub-system is in all probabilities, the higher wave length component of the band system in question. This view further explains the absence of the sub-system on our plates inasmuch as the sensitised plates employed in the investigation are not at all sensitive in the region near 9000Å. It might be useful to search for these bands in the above region with properly sensitized plates, but unfortunately this could not be done owing to such plates or the necessary dyes being not available at the present time.

In this connection, it may not be out of place to mention here, that in the literature there are some cases of heavy diatomic molecules, where only one sub-system of a doublet system has been found, the other being absent. The present bands may also be an addition to the above list, which question can only be finally settled after the search for these bands in the expected region has been carefully carried out.